AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

ICP-128

SPECTROGREEN

Analysis of Metal Impurities in Hydrochloric Acid Using ICP-OES with Dual Side-On Interface Plasma Observation

Introduction

Hydrochloric acid is an important basic chemical widely used in the industry. The largest consumption for hydrochloric acid is for steel pickling, ore processing, oil well acidizing, but it is also used in food manufacturing as an acid buffer, for cleavage of proteins or during the processing of drinking water [1]. The specific application ultimately determines the required hydrochloric acid product quality.

This report describes the methodology for the analysis of trace metal impurities in hydrochloric acid. It presents typical detection limits for a selection of relevant elements and includes studies on accuracy via the analysis of a control sample.

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a widely used method for the determination of macro and trace elements in various matrices due to its multi-element determination capability, large linear dynamic range, sensitivity and robustness.

This report demonstrates that the SPECTROGREEN has all the required analytical capabilities in terms of sensitivity, precision and accuracy to perform the analysis of metal impurities in hydrochloric acid. The SPECTROGREEN with Dual-Side-On Interface enables high precision, high stability and low detection limits.

Experimental

Instrumentation

All measurements were performed with the SPECTROGREEN ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) with dual-side-on plasma observation. It allows for an average factor 2 enhanced sensitivity compared to single radial plasma observation and achieves a sensitivity comparable to vertical torch dual view systems, while eliminating typical axial view interferences and complexity. In addition, it offers a high matrix compatibility, a large linear dynamic range and excellent precision without the need to change the plasma observation mode during analysis. The SPECTROGREEN features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CMOS detectors, the wavelength range between 165 and 770 nm can be analyzed, allowing complete spectrum capture within 3s. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later point in time.

The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the UV is achieved, allowing for the determination of non-metals as well as the use of prominent and interference free lines in this region. An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed, which ensures excellent stability of the forward power even in the case of rapidly changing sample loads.

All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions. For sample introduction, a SeaSpray nebulizer and a cyclonic spray chamber were used. The ICP operating conditions are given in Table 1.

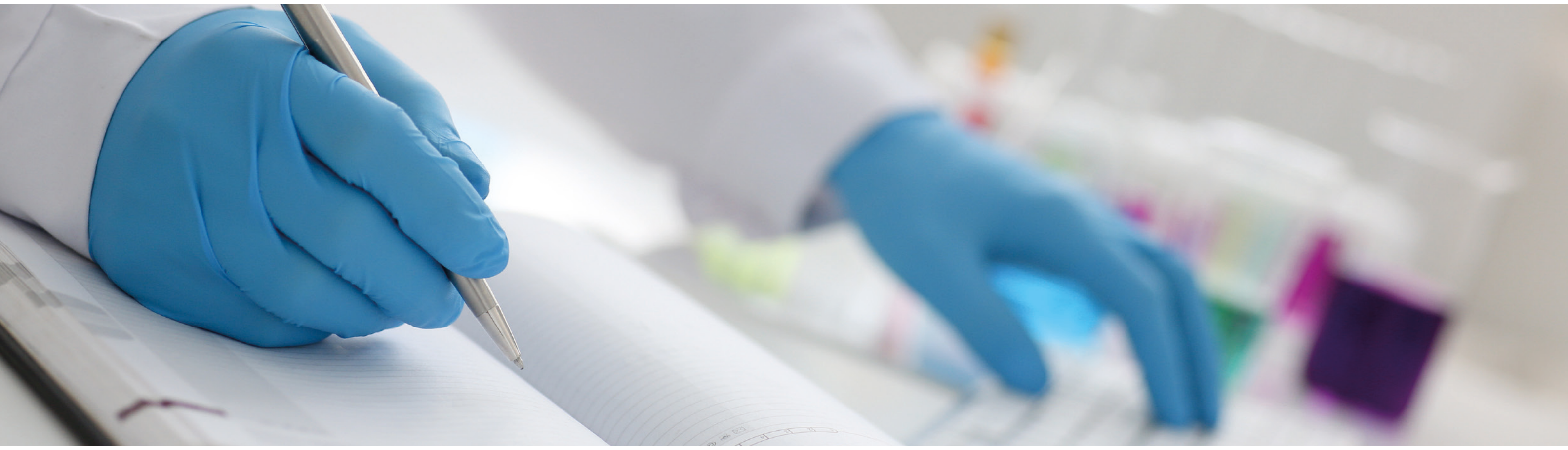
Table 2: Typical ICP operating conditions for analysis of AdBlue®

Power	1200W
Observation Mode	Dual Side-On
Coolant flow	13.0 L/min
Auxiliary flow	0.80 L/min
Nebulizer flow	0.9 L/min
Plasma Torch	Quartz, fixed, 1.8 mm Injector tube
Spray Chamber	Cyclonic
Nebulizer	SeaSpray
Sample aspiration rate	2 mL/min
Replicate read time	57 s per replicate

Sample Preparation and Calibration

Concentrated hydrochloric acid (30%) was diluted 3:2 (V/V) with deionized water. The resulting solution (20% HCl V/V) was analyzed directly without further sample preparation.

For the determination of the metals, the standard addition method was used. Standard solutions were prepared by spiking a multi-element standard solution (EPA 207, Berndt Kraft GmbH, Duisburg, Germany) into the 20% (V/V) HCl sample. Sample solutions with a spike concentration of 20, 60, and 100 μg/L were produced.



Results and Discussion

Table 2 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [2]:

$$\mathbf{LOD = 3\ RSD_b\ c/\ 100\ SBR}$$

Where:

RSD$_b$: - relative standard deviation of 10 replicates of the blank (the un-spiked sample solution) in %

c: - concentration of the standard

SBR: - signal to background ratio

Note: The 20% suprapure HCl contained mostly no trace level impurities. Where this was not the case, the RSD of the blank and the LOD was estimated using off the peak principle.

Table 2: Typical limits of detection for the selected elements and emission lines in 20% (V/V) HCl with Dual-Side-On plasma observation

Element	λ [nm]	LOD [µg/L]	Element	λ [nm]	LOD [µg/L]	Element	λ [nm]	LOD [µg/L]
Ag	328.068	0.9	**Cu**	324.754	0.9	**P**	177.495	0.9
Al	167.078	0.05	**Fe**	259.941	0.3	**Pb**	220.353	2.1
As	189.042	1.3	**Hg**	184.95	0.6	**Sb**	206.833	2.0
B	249.773	0.4	**K**	766.491	20	**Se**	196.09	2.6
Ba	455.404	0.1	**Li**	670.78	0.7	**Si**	251.612	1
Be	313.042	0.03	**Mg**	279.553	0.1	**Sn**	189.991	0.6
Ca	396.847	0.1	**Mn**	257.611	0.1	**Sr**	407.771	0.03
Cd	214.438	0.1	**Mo**	202.095	0.3	**Tl**	190.864	1.5
Co	228.616	0.3	**Na**	589.592	4.3	**V**	311.071	0.8
Cr	267.716	0.5	**Ni**	231.604	0.6	**Zn**	213.856	0.1

Accuracy

The accuracy of the method using the SPECTROGREEN with DSOI plasma observation was investigated analyzing a synthetic QC sample. As shown in Table 3, excellent recoveries are demonstrated for all elements.

Table 4: Results for the synthetic QC sample

Element	λ [nm]	Theoretical value [µg/l]	Measured conc. [µg/l]	Recovery [%]
Ag	328.068	5	5.2	104
Al	167.078	20	20.7	103
As	189.042	20	19.3	97
B	249.773	20	19.2	96
Ba	455.404	20	20.2	101
Be	313.042	20	19.9	100
Ca	396.847	20	20.7	104
Cd	214.438	20	20.1	101
Co	228.616	20	20.1	101
Cr	267.716	20	20.2	101
Cu	324.754	20	19.8	99
Fe	259.941	20	20.0	100
Hg	184.95	20	20.1	101
K	766.491	100	101.0	101
Li	670.78	20	20.2	101
Mg	279.553	20	20.3	101
Mn	257.611	20	20.0	100
Mo	202.095	20	20.3	102
Na	589.592	20	21.3	107
Ni	231.604	20	20.1	101
P	177.495	100	99.9	100
Pb	220.353	20	21.4	107
Sb	206.833	20	19.0	95
Se	196.09	20	19.8	99
Si	251.612	20	19.7	98
Sn	189.991	20	20.8	104
Sr	407.771	20	20.0	100
Tl	190.864	20	19.5	98
V	311.071	20	20.0	100
Zn	213.856	20	20.4	102

Conclusions

The SPECTROGREEN's unique radial Dual Side-On Interface (DSOI) technology represents a new approach to the critical question of plasma view design. It provides up to twice the sensitivity of conventional radial plasma- view instruments, approaching the sensitivity of recent vertical-torch dual-view designs, while avoiding their complexity challenges.

The SPECTROGREEN is a powerful tool for the analysis of trace metals contaminants in high purity hydrochloric acid. Using the DSOI interface, high sensitivity with exceptional LODs were achieved for this application, together with excellent recoveries in the low ppb range.

In combination with an autosampler, the SPECTROGREEN can be fully automated. Independent from the number of lines and elements, an analysis (including three replicates and pre-flush) can be performed in less than four minutes.

References

[1] http://www.ercoworldwide.com/index.php/products/hydrochloric-acid/

[2] Boumans, P. W. J. M. "Measuring detection limits in inductively coupled plasma emission spectrometry using the "SBR—RSDB approach"—I. A tutorial discussion of the theory." Spectrochimica Acta Part B: Atomic Spectroscopy 46.3 (1991): 431-445.

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